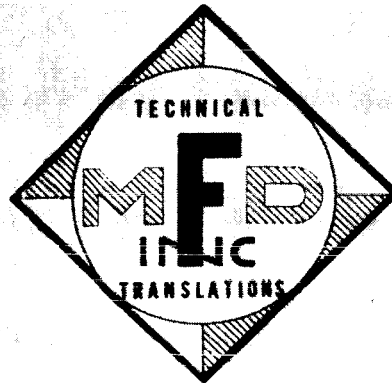Translation Number

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Russian Translation

Certain Thermodynamic Properties of a Solid Under

High Pressure

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1. Experiment shows [1] that the majority of physical, chemical and other properties of a solid body vary under the effects of high pressure. The theory of the condensed state, taking the parameters of the external high pressure into account in succession, has still not been developed within the scope of quantum mechanics nor even in classical thermodynamics. Meanwhile, consideration of the high pressure parameter in thermodynamic relations can give such dependences of certain properties of the solid on the high pressure as would differ essentially from the same dependences at atmospheric pressure. Consequently, it is of interest to investigate the influence of high pressure on the basis of ordinary thermodynamics and statistics; for example, the influence on the spectrum of the thermal oscillations of the atoms or ions, the coefficient of thermal broadening and compressibility of the crystal lattice.

2. Let us consider, as the first problem, the influence of high pressure on the spectrum of the elastic atom-oscillations of a linear, monatomic chain of a solid. First of all, the influence of compression causes a decrease in the interatomic distance for which the magnitude can be represented by an expansion in powers of a certain small parameter $\varkappa p$:

(1)
$$a(p) = a_o + a_o' \varkappa p + \frac{1}{2} a_o'' (\varkappa p)^2 + \ldots$$

where $a(p)$ and a_o are the interatomic distance at the pressure p and at atmospheric, respectively; $\varkappa$ is the linear compressibility. Inasmuch as the the product $\varkappa p$ is known to be small up to very high pressures $(p \not< 10^5 \frac{kg}{cm^2})$

because of the smallness of the compressibility $(\varkappa \sim 10^{-6}$ $kg^{-1} \cdot cm^2)$, then, as it is easy to show, the expansion (1), having been limited to the first two terms, can be reduced to:

(1a)
$$a(f) \simeq a_0(1 - |\varkappa_f|f)$$

Here $f = p \cdot 10^{-15}$ is the external pressure in dynes per atomic chain $(10^{-15}$ cm^2 is the area of the cross-section of the atomic chain); $\varkappa_f$ is the chain compressibility. For example, $\varkappa \sim 10^{-6}-10^{-5}$ $kg^{-1} \cdot cm^2$ for $p \sim 10^4$ $kg \cdot cm^{-2}$ [1];

$$\varkappa_f = -\frac{1}{a_0}\frac{\partial a(f)}{\partial f} = \varkappa \cdot 10^9 = 10^3 \text{ to } 10^4 \text{ per dyne and } \varkappa_f f \sim 10^{-2}.$$

In order to make possible the approximate qualitative comparison of the theoretical results on determining the intrinsic oscillation spectrum of a linear chain under high pressure with experimental results, it is necessary to know the form of the potential of the interaction between the atoms. On the basis of [2,3] for very high pressures, which are of interest, the greatest variation in the potential energy is specified by the variation of the energy arising during the overlapping of the undeformed electron shells of the ions. It can be shown by analogy with [3] that the ion interaction potential in a chain which takes into account both the electrostatic repulsion and the overlapping of the electron shells will have the form:

(2)
$$U(r) = e^{-\gamma r}(A + Br + Cr^2 + Dr^{-1})$$

where, according to [3], $A \sim 3 \cdot 10^{-11}$ erg; $B \sim 0.7 \cdot 10^{-11}$ erg.cm^{-1}; $C \sim 0.1 \cdot 10^{-11}$ erg$\cdot cm^{-2}$; $D \sim 13 \cdot 10^{-11}$ erg$\cdot cm$; r is the interatomic spacing in atomic units; $\gamma = 2.9$ atomic units.

The maximum frequency of the elastic oscillations of a linear chain compressed by f dynes equals:

(3)
$$\nu_{max} = \frac{1}{2\pi}\sqrt{\frac{a(f)}{m}}$$

where m is the mass of the atom; $\alpha(f)$ is the elastic coupling coefficient of the atoms in the chain which equals:

(4)
$$\alpha(f) = \frac{1}{2}\left[\frac{\partial^2 U(r)}{\partial r^2}\right]_r \longrightarrow a(f)$$

Substituting (2) into (4) and neglecting small terms, we obtain:

(5)
$$\alpha(f) \simeq \alpha_o(1 + |\varkappa_f|f)\exp(\gamma a_o|\varkappa_f|f)$$

where α_o is the elastic coupling coefficient at atmospheric pressure.

Since the Debye temperature is determined according to the formula $\theta = \frac{\hbar\nu_{max}}{k}$, then we find from (3) and (5):

(6)
$$\theta(f) \simeq \theta_o(1 + |\varkappa_f|f)\exp(\frac{1}{2}\gamma a_o|\varkappa_f|f)$$

where $\theta(f)$ and θ_o are the Debye temperature at the pressure f and at atmospheric pressure, respectively.
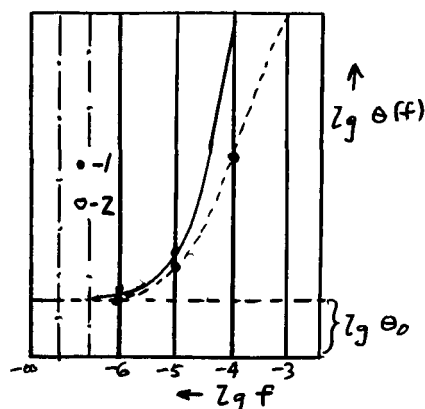
The existence of the exponential factor in (6) leads to a sharp increase in the Debye temperature as the external pressure increases. This is specified by a sharp increase in the energy because of the overlapping of the electron shells as the ions approach under the action of the high pressure, which leads to a decrease in the amplitude of their oscillations and, therefore, to an increase in frequency.

The exponential term in (6) can be expanded into series for small values of the $|\varkappa_f|f$ parameter. This yields:

(6a)
$$\theta(f) \simeq \theta_o(1 + d|\varkappa_f|f)$$

where $d = 1 + \gamma a_o$. According to (6), we obtain, respectively, for $p = 10^3$, 10^4, 10^5 kg·cm^{-2} and $\gamma = 2.9$ atomic units: $\theta(f) = 1.0034$, 1.034, and $1.34\theta_o$ (see sketch). The variation of the compressibility with the pressure is not taken into account in (6). When this variation is taken into account, the

growth of $\Theta(f)$ as the pressure increases will be slower than is shown, qualitatively on the sketch by the dashed line.

3. The maximum frequency of the elastic oscillations of ions of a three-dimensional crystal lattice of cubical symmetry at the pressure p is determined, as is known, by the expression:

Dependence of Debye temperature on high pressure
1 - without considering $\frac{d|\varkappa|}{df}$
2 - considering $\frac{d|\varkappa|}{df}$

$$(7) \qquad \nu_{max}(p) = \left[\frac{3}{4}\, \frac{3N}{V(p)}\, \frac{v_t^3 v_l^3}{v_t^3 + v_l^3}\right]^{\frac{1}{3}}$$

where $3N$ is the number of atoms in the crystal lattice; $V(p)$ is the crystal volume; v_t and v_l are the propagation velocities, respectively, of the transverse and longitudinal elastic oscillations in the crystal. Considering v_t and v_l to be equal in the case of an isotropic cubical crystal and using (1a) and also the obvious condition:

$$V(p) = V_o(1 - |K|p)$$

where K is the magnitude of the volume compressibility which equals $\simeq 3\varkappa$; V_o is the initial volume, we obtain an expression for the dependence of the Debye temperature on high pressure:

$$(8) \qquad \Theta(p) = \Theta_o \frac{1 + \frac{1}{2}|\varkappa|p}{(1 - 3|\varkappa|p)^{\frac{1}{3}}}\, \exp(\frac{1}{2}\gamma a_o |\varkappa|p)$$

Formula (8) becomes, for small values of $|\varkappa|p$:

$$(8a) \qquad \Theta(p) \simeq \Theta_o(1 + g|\varkappa|p)$$

where $g = \frac{1}{2}(3 + \gamma a_o)$. Since the parameter g is essentially a positive quantity, then from (8) and (8a) there follows that $\Theta(p)$ increases as the external pressure increases.

On the basis of (8a), the coefficient of Debye temperature variation with pressure equals:

$$(9) \qquad \sigma = \frac{1}{\theta_o} \frac{d\theta(p)}{dp} = g|\varkappa| \left(1 + \frac{1}{|\varkappa|} \frac{d\varkappa}{dp} p\right)$$

According to [1]:

$$\frac{1}{|\varkappa|} \frac{d\varkappa}{dp} \sim 10^{-5} \text{ kg}^{-1} \cdot \text{cm}^2$$

consequently, the increase in σ, for example for $p = 10^4$ kg·cm^{-2}, is several percent but the growth of σ will be very significant for $p = 10^5$ kg·cm^{-2}.

4. Let us use the formulas obtained to derive a dependence of the linear coefficient of the thermal expansion of a solid $\delta(f)$ on high pressure. As is known [4], $\delta(f)$ for atomic chains taking the anharmonicity of elastic oscillations into account can be represented thus:

$$(10) \qquad \delta(f) = \frac{\beta(f) \ k}{a(f) \ \alpha^2(f)}$$

where $\beta(f) = \frac{1}{6}\left[\frac{\partial^3 U}{\partial r^3}\right]_{r \to a(f)}$ is the coefficient of anharmonic coupling of the atoms in the chain; k is the Boltzmann constant. Substituting (1a), (2) and (5) in (10), we obtain:

$$(11) \qquad \delta(f) = \delta_o(1 - 2|\varkappa_f|f) \exp(-\gamma a_o |\varkappa_f|f)$$

where δ_o is the coefficient of linear expansion of the atomic chain at atmospheric pressure. Again we have for small $|\varkappa_f|f$

$$(11a) \qquad \delta(f) \simeq \delta_o(1 - |c||\varkappa_f|f)$$

where $c = 2 + \gamma a_o$ is substantially a positive quantity for values of a_o and γ taken. From (11) and (11a) there follows that the linear coefficient of thermal expansion of a solid decreases as the pressure increases, which agrees with experiment, qualitatively, for all known metals [1].

The variation of the thermal expansion coefficient with pressure equals, on

the basis of (11a) without taking into account the compressibility variation with increased pressure:

$$(12) \qquad \frac{1}{\delta_o} \frac{d\delta(f)}{df} = - c|\varkappa_f|$$

The negative sign on the right side of (12) indicates a decrease in $\delta(f)$ as the pressure increases.

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